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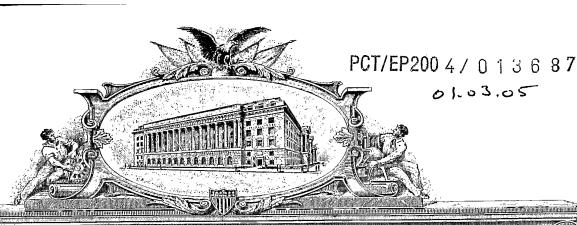
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APPLICATION NUMBER: 60/526,609 FILING DATE: December 04, 2003

By Authority of the

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P. R. GRANT

Certifying Officer

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PROVISIONAL APPLICATION COVER SHEET

PF55118/Za

This is a request for filing a PROVISIONAL APPLICATION under 35 USC 111(b).

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2. TITLE OF THE INVENTION:

USE OF N-ARYLHYDRAZINE DERIVATIVES FOR COMBATING PESTS

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- 4. ENCLOSED APPLICATION PARTS:
 - [X] Specification
- 30 pages
- [] Drawings
- ___ sheets
- [X] Claims
- 9 claims
- METHOD OF PAYMENT
 - [X] A check in the amount of \$160.00 is attached to cover the required Provisional filing fee.
 - [X] The commissioner is hereby authorized to charge any deficiency in fees to Deposit Account 11.0345.
- 6. The invention was <u>not</u> made by an agency of the United States Government or under a contract with an agency of the United States Government.

Respectfully submitted,

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The present invention relates to the use of hydrazine derivatives of formula I:

$$\bigvee_{R=A}^{n} \bigvee_{N=Q}^{R} \qquad (I)$$

5

wherein

Q

$$N = <_{R^3}^{NR^1R^2}$$

$$<_{\mathbf{R}^3}^{\mathsf{NR}^1\mathbf{R}^2}$$
 , $\mathsf{N} = <_{\mathbf{R}^3}^{\mathsf{X}^1}$, or

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 X^1 is chlorine, bromine, or fluorine;

R¹, R² are each independently hydrogen, C₁-C₁₀-alkyl, C₃-C₁₀-alkenyl, C₅-C₁₀-alkynyl, or C₃-C₁₂-cycloalkyl, C₁-C₆-alkylamino, di(C₁-C₆-alkyl)-amino, C₁-C₆alkylcarbonylamino, C₁-C₆-alkylsulfonyl, or C₁-C₆-alkylsulfinyl, wherein the carbon atoms in these groups may be substituted with

> 1 to 3 halogen, hydroxy, nitro, cyano, amino, mercapto, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-haloalkylthio, C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfinyl, C₁-C₆-haloalkylsulfonyl, C₁-C₆-haloalkylsulfinyl, or C₃-C₆cycloalkyl which may be substituted with 1 to 3 R" groups, or

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R[#] is halogen, cyano, nitro, hydroxy, mercapto, amino, C₁-C₈-alkoxy, C₂-C₆-alkenyloxy, C₂-C₆-alkynyloxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, or C₁-C₆-haloalkylthio, C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfinyl, C₁-C₆alkylamino, di(C1-C6alkyl)-amino, C1-C6-alkylcarbonyl, C1-C6alkoxycarbonyl, or di(C₁-C₆)-alkylaminocarbonyl;

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formyl, C₁-C₅-alkylcarbonyl, C(=0)NR^aR^b, CO₂R^c, R^d, R^e, phenyl which may be substituted with 1 to 3 R# groups, or pyridyl which may be substituted with 1 to 3 R# groups,

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R^a, R^b, R^c are each independently hydrogen or C₁-C₄-alkyl which may be substituted with 1 to 3 groups R#;

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is NR^IR^I or Rd

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$$N \stackrel{(CH_2)_p}{\sim} X_p$$

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RI, RI are each independently hydrogen or C₁-C₄-alkyl which may be substituted with 1 to 3 groups R";

p, m are each independently 0, 1, 2, or 3, with the proviso that p and m are not both 0.

X is oxygen, sulfur, amino, C₁-C₄-alkylamino, or phenylamino, or, if p is 0 then X can also be phenoxy or C₁-C₆-alkoxy;

ľ is 0 or 1;

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R is

Rk, Rq are each independently hydrogen or C1-C4-alkyl which may be substituted with 1 to 3 groups R#; or

R1 and R2 may be taken together to form a ring represented by the structure

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p,m are 1, 2 or 3;

is oxygen, sulfur, amino, C₁-C₄-alkylamino, phenylamino, or methylene;

Z is C₁-C₄-alkyl or phenyl;

25 \mathbf{R}^3 is hydrogen, C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₃-C₁₂-cycloalkyl, wherein the carbon atoms in these groups may be partially or fully halogenated or substituted with

> 1 to 3 cyano, nitro, hydroxy, mercapto, amino, C₁-C₆-alkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-alkylamino, di(C₁-C₆-alkyl)-amino, C₁-C₆-alkylthio, C₁-C₆-alkyl alkylsulfonyl, or C₁-C₆-alkylsulfinyl groups, wherein the carbon atoms in these groups may be substituted by

1 to 3 halogen atoms, a 5- to 6-membered aromatic ring system which may contain 1 to 4 heteroatoms selected from oxygen, sulfur and nitrogen and which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C₁-C₆-alkyl, C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, C₁-C₆-

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alkylsulfinyl, C₁-C₆-alkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms, or

phenoxy, which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C_1 - C_6 -alkyl, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylsulfinyl, C_1 - C_6 -alkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms, or

a 3- to 6-membered saturated or partially unsaturated ring system which contains 1 to 3 heteroatoms selected from oxygen, sulfur and nitrogen and which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C_1 - C_6 -alkyl, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylsulfonyl, C_1 - C_6 -alkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms,

a 3- to 6-membered saturated or partially unsaturated ring system which contains 1 to 3 heteroatoms selected from oxygen, sulfur and nitrogen and which is unsubstituted or substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C_1 - C_6 -alkyl, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylsulfonyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms;

- A, R⁴ are each independently hydrogen or C₁-C₆-alkyl, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkyl)-aminocarbonyl, wherein the carbon atoms in the these groups may be substituted with 1 to 3 groups R^{*};
 - A is C-R⁵ or N;
 - B is C-R⁶ or N;
- 30 W is C-R⁷ or N:

with the proviso that one of A, B and W is other than N;

- R⁵, R⁶, R⁷ are each independently hydrogen, halogen, nitro, cyano, amino, mercapto, hydroxy, C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-alkylamino, di(C₁-C₆-alkyl)-amino, C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, or C₁-C₆-alkylsulfinyl, wherein the carbon atoms in these groups may be substituted with 1 to 3 groups R[#]
- a 5- to 6-membered aromatic ringsystem which may contain 1 to 4 het-40 eroatoms selected from oxygen, sulfur and nitrogen and which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C₁-C₅alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkylthio, C₁-C₆-haloalkylthio, C₁-C₆-

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alkylsulfonyl, C_1 - C_6 -alkylsulfinyl, C_1 - C_6 -haloalkylsulfonyl, C_1 - C_6 -haloalkylsulfinyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, mercapto, hydroxy, amino, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted with 1 to 3 groups R^* :

is hydrogen, halogen, cyano, nitro, amino, hydroxy, mercapto, C₁-C₆-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-alkylamino, di(C₁-C₆)-alkylamino, C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, or C₁-C₆-alkylsulfinyl, wherein the carbon atoms in these groups may be substituted with 1 to 3 groups R*:

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n is 0, 1, or 2;

or the enantiomers or diastereomers, salts or esters thereof,

15 for combating non-crop pests.

The invention also relates to a method for controlling pests selected from the above orders comprising contacting the pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of compounds of formula 1.

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The invention also relates to compositions for controlling pests of the above orders.

Typical problems arising with the use of presently available non-crop pest controllers with a broad spectrum of activity such as pyrethroids are e.g. resistance of pests or unfavorable toxicological properties. Accordingly, there is a need to provide new and improved non-crop pest controllers that overcome these problems.

It is therefore an object of the present invention to provide new non-crop pest controllers exhibiting an enhanced pesticidal spectrum of action.

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It is also an object of the present invention to provide a method for controlling pests selected from the above orders.

We have found that these objects are achieved by use of compounds of formula I and compositions comprising them.

The hydrazine derivatives of formula I which can be used according to the invention are known from EP-A 604 798. This document relates to plant protection in the agricultural filed and discloses the insecticidal and acaricidal activity of compounds of fomula I against crop pests of the Coleoptera, Lepidoptera and Acarina orders.

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The compounds of formula I can be prepared according to preparation methods described or referenced in EP-A 604 798 or modifications thereof.

In the definition of formula I shown above, the substituents have the following meanings:

"Halogen" will be taken to mean fluoro, chloro, bromo and iodo.

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group having 1 to 10 carbon atoms, especially C₁-C₆-alkyl such as methyl,
ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl,
pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl,
hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl,
2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2methylpropyl.

The term "haloalkyl" as used herein refers to a straight-chain or branched alkyl groups
having 1 to 10 carbon atoms (as mentioned above), where some or all of the hydrogen
atoms in these groups may be replaced by halogen atoms as mentioned above, for
example C₁-C₂-haloalkyl, such as chloromethyl, bromomethyl, dichloromethyl, triichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl;

"Alkoxy" refers to straight-chain or branched alkyl group having 1 to 4 or 6 carbon atoms (as mentioned above) bonded through an oxygen linkage, at any bond in the alkyl group. Examples include methoxy, ethoxy, propoxy, and isopropoxy.

Likewise, the terms "alkylthio", "alkylamino", "dialkylamino", "alkylsulfonyl", and alkylsulfinyl" refer to straight-chain or branched alkyl group having 1 to 4 or 6 carbon atoms (as mentioned above) bonded through a sulfur-, -NH-, -N-, -S(=O)₂-, or S(=O)- linkage, respectively.

The term "alkenyl" as used herein intends a branched or unbranched unsaturated hydrocarbon group having 3 to 10 carbon atoms and a double bond in any position, such as C_3 - C_6 alkenyl such as 1-propenyl, 2-propenyl, 1-methyl-ethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl; 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 3-methyl-1-butenyl, 3-methyl-2-butenyl, 3-methyl-2-butenyl, 3-methyl-1-butenyl, 3-

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methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;

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- "Cycloalkyl" refers to a monocyclic 3- to 6-, 8-, 10- or 12-membered saturated carbon atom rings, e.g. C₃-C₆-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.
- A 5- to 6-membered aromatic ring system containing 1 to 4 heteroatoms selected from 20 oxygen, sulfur and nitrogen, intends e.g. 5-membered hetaryl, containing 1 to 4 nitrogen atoms or 1 to 3 nitrogen atoms and 1 sulfur or oxygen atom, e.g. furyl, thienyl, pyrrolyl, isoxazolyl, isothiazolyl, pyrazolyl, oxazolyl, thiazolyl, imidazolyl, oxadiazolyl, thiadiazolyl, oxadiazolyl, triazolyl, and tetrazolyl; or 6-membered hetaryl, containing 1 to 4 nitrogen atoms or 1 to 3 nitrogen atoms and 1 sulfur or oxygen atom, e.g. 2-pyridinyl, 25 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl;
- a 3- to 6-membered saturated or partially unsaturated ring system which contains 1 to 30 3 heteroatoms selected from oxygen, sulfur and nitrogen intends e.g. a saturated 3- to 6-membered ringsystem containing 1 to 3 heteroatoms selected from nitrogen and oxygen, such as aziridine, pyrrolidine, tetrahydrofuran, tetrahydropyran, or piperidine.
- With respect to the intended use of the compounds of formula I, particular preference is 35 given to the following meanings of the substituents, in each case on their own or in combination:
 - Preference is given to compounds of formula I wherein A denotes C-R⁵.
- Moreover, preference is given to compounds of formula I wherein B denotes C-R⁵. 40
 - Preference is also given to compounds of formula I wherein W denotes C-R⁷.

Particular preference is given to compounds wherein A denotes C-R⁵, B denotes C-R⁶, and W denotes C-R⁷.

Moreover, preference is given to compounds of formula I wherein R^δ is halogen or C₁-C₆-haloalkyl, with halogen, especially chlorine, being most preferred.

Preference is also given to compounds of formula I wherein R⁶ is hydrogen or halogen, especially hydrogen.

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Preference is further given to compounds of formula I wherein R^7 is halogen or C_1 - C_6 -haloalkyl, preferably C_1 - C_6 -haloalkyl, especially trifluoromethyl.

Moreover, preference is given to compounds of formula I wherein Y is halogen or C₁-C₆-haloalkyl. Particular preference is given to compounds of formula I wherein Y is halogen, especially chlorine.

Preference is given to compounds of formula I wherein n is 1.

20 Preference is also given to compounds of formula I wherein Q denotes -N=[C(NR¹R²)R³].

Moreover, preference is given to compounds of formula I wherein X1 is chlorine.

25 Preference is also given to compounds of formula I wherein R denotes C₁-C₆-alkyl or hydrogen.

Preference is also given to compounds of formula I wherein R¹ and R² each independently are hydrogen, C₁-C₁₀-alkyl, or C₃-C₁₀-cycloalkyl.

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Moreover, preference is given to compounds of formula I wherein R^1 and R^2 each independently are hydrogen, C_1 - C_4 -alkyl, or C_3 - C_5 -cycloalkyl.

Moreover, preference is given to compounds of formula I wherein R³ is unsubstituted C₁-C₁₀-alkyl or C₃-C₁₀-cycloalkyl, which may be substituted with 1 to 5 halogen atoms and/or 1-3 C₁-C₆-alkyl groups.

Particularly preferred are compounds of formula I wherein R³ is tert.-butyl.

Moreover, particularly preferred are compounds of formula I wherein R³ is cyclopropyl which may be substituted with C₁-C₆-alkyl or halogen, especially 1-methyl-2,2-dichlorocyclopropyl.

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Moreover, preference is given to compounds of formula I wherein R⁴ is hydrogen or C₁-C₆-alkyl.

5 Particular preference is given to N-ethyl-2,2-dimethylpropionamide,2-(2,6-dichloroα, α, α-trifluoro-p-tolyl) hydrazone and N-Ethyl-2,2-dichloro-1-methylcyclopropanecarboxamide, 2-(2,6-dichloro- α , α , α -trifluoro-p-tolyl)hydrazone.

Furthermore, particular preference with respect to the use in the present invention is 10 given to the compound of formula I-1 (N-ethyl-2,2-dimethylpropionamide,2-(2,6dichloro- α , α , α -trifluoro-p-tolyl)-hydrazone):

Moreover, particular preference with respect to the use in the present invention is given to the compound of formula 1-2 (N-Ethyl-2,2-dichloro-1-

15 methylcyclopropanecarboxamide, 2-(2,6-dichloro- α , α , α -tri-fluoro-p-tolyl)hydrazone):

The compounds of formula I are suitable for combating non-crop pests in the protection of stored products and of materials, in the hygiene field, and also in forestry and agriculture. They are active against all or some stages of development.

Non-crop pests are commonly understood as pests from the classes Chilopoda and Diplopoda, from the orders Isoptera, Blattaria (Blattodea), Diptera, Dermaptera, Hemiptera, Thysanoptera, Hymenoptera, Orthoptera, Siphonaptera, Thysanura, Phthiraptera, Mesostigmata, Prostigmata, Astigmata, and Ixodida and from the families Saturniidae, Pyralididae, Gelechiidae, Meloidae.

The compounds of the formula I are especially suitable for efficiently combating the following pests:

30 centipedes (Chilipoda), e.g. Scutigera coleoptrata,

millipedes (Diplopoda), e.g. Narceus spp.,

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termites (Isoptera), e.g. Calotermes flavicollis, Leucotermes flavipes, Heterotermes aureus, Reticulitermes flavipes, Reticulitermes virginicus, Reticulitermes lucifugus and Termes natalensis, Coptotermes formosanus

5 cockroaches (Blattaria - Blattodea), e.g. Blattella germanica, B. asahinae, Periplaneta americana, Periplaneta japonica, Periplanata brunnea, Periplanata fuligginosa, P. australasiae, and Blatta orientalis

flies, mosquitoes (Diptera), e.g. Aedes aegypti, Aedes albopictus, Aedes vexans, Anastrepha ludens, Anopheles maculipennis, Anopheles crucinas, An. albimanus, An. 10 Gambiae, An. freeborni, An. leucosphyrus, An. minimus, An. quadrimaculatus, Calliphora vicina, Ceratitis capitata, Chrysomya bezziana, Chrysomya hominivorax, Chrysomya macellaria, Chrysomya bezziana, Chrysops discalis, C. silacea, C. atlanticus, Cochliomyia hominivorax, Contarinia sorghicola, Cordylobia anthropophaga, Culicoides 15 furens, Culex pipiens, Culex nigripalpus, C. quinquefasciatus, C. tarsalis, Culiseta inornata, C. melanura, Dacus cucurbitae, Dacus oleae, Dasineura brassicae, Dermatobia hominis, Fannia canicularis, Gasterophilus intestinalis, Glossina morsitans, Glossina palpalis, G. fuscipes, G. tachinoides, Haematobia irritans, Haplodiplosis equestris, Hippelates spp., Hylemyla platura, Hypoderma lineata, Leptoconops torrens, Liriomyza 20 sativae, Liriomyza trifolii, Lucilia caprina, Lucilia cuprina, Lucilia sericata, Lycoria pectoralis, Mansonia titillanus, Mayetiola destructor, Musca domestica, Muscina stabulans, Oestrus ovis, Oscinella frit, Pegomya hysocyami, Phorbia antiqua, Phorbia brassicae, Phorbia coarctata, Phlebotomus argentipes, Psorophora columbiae, P. discolor, Prosimuliim mixtum, Rhagoletis cerasi, Rhagoletis pomonella, Sarcophaga haemorrhoidalis, 25 Sarcophaga sp., Simuliim vittatum, Stomoxys calcitrans, Tabanus bovinus, Tabanus atratus, T. lineola, T. similis, Tipula oleracea, and Tipula paludosa

Earwigs (Dermaptera), e.g. forficula auricularia,

30 true bugs (Hemiptera), e.g. Acrosternum hilare, Blissus leucopterus, Cyrtopeltis notatus, Dysdercus cingulatus, Dysdercus intermedius, Eurygaster integriceps, Euschistus impictiventris, Leptoglossus phyllopus, Lygus lineolaris, Lygus pratensis, Nezara viridula, Piesma quadrata, Solubea insularis , Thyanta perditor, Acyrthosiphon onobrychis, Adelges laricis, Aphidula nasturtii, Aphis fabae, Aphis forbesi, Aphis pomi, Aphis gos-35 sypii, Aphis grossulariae, Aphis schneideri, Aphis spiraecola, Aphis sambuci, Acyrthosiphon pisum, Aulacorthum solani, Brachycaudus cardui, Brachycaudus helichrysi, Brachycaudus persicae, Brachycaudus prunicola, Brevicoryne brassicae, Capitophorus horni, Cerosipha gossypii, Chaetosiphon fragaefolii, Cryptomyzus ribis, Dreyfusia nordmannianae, Dreyfusia piceae, Dysaphis radicola, Dysaulacorthum pseudosolani, 40 Dysaphis plantaginea, Dysaphis pyri, Empoasca fabae, Hyalopterus pruni, Hyperomyzus lactucae, Macrosiphum avenae, Macrosiphum euphorbiae, Macrosiphon rosae, Megoura viciae, Melanaphis pyrarius, Metopolophium dirhodum, Myzodes persicae,

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Myzus ascalonicus, Myzus cerasi, Myzus varians, Nasonovia ribis-nigri, Nilaparvata lugens, Pemphigus bursarius, Perkinsiella saccharicida, Phorodon humulí, Psylla mali, Psylla piri, Rhopalomyzus ascalonicus, Rhopalosiphum maidis, Rhopalosiphum padi, Rhopalosiphum insertum, Sappaphis mala, Sappaphis mali, Schizaphis graminum, Schizoneura lanuginosa, Sitobion avenae, Trialeurodes vaporariorum, Toxoptera aurantiiand, Viteus vitifolii, Cimex lectularius, C. hemipterus, Reduvius senilis, Triatoma

spp., and Arilus critatus.

thrips (Thysanoptera), e.g. Frankliniella fusca, Frankliniella occidentalis, Frankliniella 10 tritici, Scirtothrips citri, Thrips onyzae, Thrips palmi and Thrips tabaci,

ants, bees, wasps, sawflies (Hymenoptera), e.g. Athalia rosae, Atta cephalotes, Atta sexdens, Atta texana, Crematogaster spp., Hoplocampa minuta, Hoplocampa testudinea, Monomorium pharaonis, Solenopsis geminata, Solenopsis invicta, S. richteri, S. xyloni, Pogonomyrmex barbatus, Pogonomyrmex californicus, Dasymutilla occidentalis, Bombus spp. Vespula squamosa, Paravespula vulgaris, P. pennsylvanica, P. germanica, Dolichovespula maculata, Vespa crabro, Polistes rubiginosa, Camponotus floridanus, and Linepitheum humile,

20 crickets, grasshoppers, locusts (Orthoptera), e.g. Acheta domestica, Forficula auricularia, Gryllotalpa gryllotalpaLocusta migratoria, Melanoplus bivittatus, Melanoplus femurrubrum, Melanoplus mexicanus, Melanoplus sanguinipes, Melanoplus spretus, Nomadacris septemfasciata, Schistocerca americana, Schistocerca peregrina, Stauronotus maroccanus and Tachycines asynamorus,

fleas (Siphonaptera), e.g. Ctenocephalidea felis, C. canis, Xenopsylla cheopis, Pulex irritans, Tunga penetrans, and Nosopsyllus fasciatus

silverfish, firebrat (Tysanura), e.g. Lepisma saccarina and Thermobia domestica

lice (Phthiraptera), e.g. Pediculus humanus capitis, Pediculus humanus corporis, Pythirus pubis, Haematopinus eurysternus, Haematopinus suis, Linognathus vituli and Solenopotes capillatus

35 Mesostigmata, e.g. Ornithonyssus bacoti and Dermanyssus gallinae,

Prostigmata, e.g. Pymotes tritici,

Astigmata, e.g. Acarus siro,

ticks (Ixodida), e.g. Phipicephalus sanguineus,

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Saturniidae, e.g. Automeris io,

Urticating caterpillars (Lymantriidae), e.g. Lymantria dispar and Euproctis chrysorrhoea,

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Pyralididae, e.g. Plodia interpunctella, and Ephestia kuhniella,

Gelechiidae, e.g. Sitotroga cerealella,

10 Meloidae, e.g. Epicauta fabricii and E. vittana,

> The compounds of formula I and compositions containing them are particularly useful for the control of pests of the orders Isoptera, Blattaria (Blattodea), Diptera, Dermaptera, Hemiptera, Thysanoptera, Hymenoptera, Orthoptera, Siphonaptera, Thysanura, and Phthiraptera.

Moreover, the compounds of formula I and compositions containing them are especially useful for the control of Isoptera, Diptera, Blattaria (Blattodea), Hymenoptera, and Siphonaptera.

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In particular, the compounds of formula I and compositions containing them are useful for the control of Isoptera (hodotermitidae, kalotermitidae, rhinotermitidae, termitidae), Diptera (tipulidae, blephariceridae, deuterophlebiidae, pachyneuridae, trichceridae, culicidae, simuliidae, ceratopogonidae, chironomidae, tabanidae, rhagionidae, mydidae, hilarimorphidae, tephritidae, braulidae, chloropidae, tethinidae, muscidae, calliphoridae, oestridae, sarcophagidae, rhinophoridae, tachnidae, hippoboscidae), Blattaria/Blattodea (cryptocercidae, blattidae, polyphagidae, blattellidae), Hymenoptera (xyelidae, argidae, cimbicidae, tenthredinidae, anaxyelidae, cephidae, aphidiidae, formicidae, vespoidae, sphecidae), and Siphonaptera (pulicidae, rhopalopsyllidae, ceratophyllidae).

For use according to the present invention, the compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; it is intended to ensure in each case a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries, which are suitable, are essentially:

water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone),

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pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used.

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- carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. highly disperse silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.
- Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with
 formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, strongly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for spreading and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

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In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

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The following are examples of formulations: 1. Products for dilution with water

A Soluble concentrates (SL)

10 parts by weight of a compound according to the invention are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active ingredient dissolves upon dilution with water.

B Dispersible concentrates (DC) -

20 parts by weight of a compound according to the invention are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C Emulsifiable concentrates (EC)

15 parts by weight of a compound according to the invention are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

D Emulsions (EW, EO)

40 parts by weight of a compound according to the invention are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifier (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

30 E Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of a compound according to the invention are comminuted with addition of dispersant, wetters and water or an organic solvent to give a fine active ingredient suspension. Dilution with water gives a stable suspension of the active ingredient.

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F Water-dispersible granules and water-soluble granules (WG, SG) 50 parts by weight of a compound according to the invention are ground finely with addition of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower,

40 fluidized bed). Dilution with water gives a stable dispersion or solution of the active ingredient.

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G Water-dispersible powders and water-soluble powders (WP, SP)
75 parts by weight of a compound according to the invention are ground in a rotor—stator mill with addition of dispersant, wetters and silica gel. Dilution with water gives a stable dispersion or solution with the active ingredient.

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- 2. Products to be applied undiluted ...
- H Dustable powders (DP)

5 parts by weight of a compound according to the invention are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I Granules (GR, FG, GG, MG)

0.5 parts by weight of a compound according to the invention is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray drying or the fluidized bed. This gives granules to be applied undiluted.

J ULV solutions (UL)

10 parts by weight of a compound according to the invention are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

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The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, eg. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; it is intended to ensure in each case the finest possible distribution of the active ingredients according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier.

Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active ingredient concentrations in the ready-to-use products can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

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The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even to apply the active ingredient without additives.

- 5 Various types of oils, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate just immediately prior to use (tank mix). These agents usually are admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.
- 10 The compounds of formula I are effective through both contact (via soil, glass, wall, bed net, carpet, plant parts or animal parts), and ingestion (bait, or plant part).

According to a preferred embodiment of the invention, the compounds of formula I are prepared into a bait preparation.

For use against ants, termites, wasps, flies, mosquitos, crickets, or cockroaches, compounds of formula I are preferably used in a bait composition.

The bait can be a liquid, a solid or a semisolid preparation (e.g. a gel). Solid baits can 20 be formed into various shapes and forms suitable to the respective application e.g. granules, blocks, sticks, disks. Liquid baits can be filled into various devices to ensure proper application, e.g. open containers, spray devices, droplet sources, or evaporation sources. Gels can be based on aqueous or oily matrices and can be formulated to particular necessities in terms of stickyness, moisture retention or aging characteristics.

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The bait employed in the composition is a product which is sufficiently attractive to incite insects such as ants, termites, wasps, flies, mosquitos, crickets etc. or cockroaches to eat it. The attractiveness can be manipulated by using feeding stimulants or sex pheromones. Food stimulants are chosen, for example, but not exclusively, from animal and/or plant proteins (meat-, fish- or blood meal, insect parts, egg yolk), from fats and oils of animal and/or plant origin, or mono-, oligo- or polyorganosaccharides, especially from sucrose, lactose, fructose, dextrose, glucose, starch, pectin or even molasses or honey. Fresh or decaying parts of fruits, crops, plants, animals, insects or specific parts thereof can also serve as a feeding stimulant. Sex pheromones are known to be more insect specific. Specific pheromones are described in the literature and are known to those skilled in the art.

Formulations of compounds of formula I as aerosols (e.g in spray cans), oil sprays or pump sprays are highly suitable for the non-professional user for controlling pests such as flies, fleas, ticks, mosquitos or cockroaches. Aerosol recipes are preferably composed of the active compound, solvents such as lower alcohols (e.g. methanol, etha-

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nol, propanol, butanol), ketones (e.g. acetone, methyl ethyl ketone), paraffin hydrocarbons (e.g. kerosenes) having boiling ranges of approximately 50 to 250 °C, dimethyl-fomaamide, N-methylpyrrolidone, dimethyl sulphoxide, aromatic hydrocarbons such as toluene, xylene, water, furthermore auxiliaries such as emulsifiers such as sorbitol monooleate, oleyl ethoxylate having 3-7 mol of ethylene oxide, fatty alcohol ethoxylate, perfume oils such as ethereal oils, esters of medium fatty acids with lower alcohols, aromatic carbonyl compounds, if appropriate stabilizers such as sodium benzoate, amphoteric surfactants, lower epoxides, triethyl orthoformate and, if required, propellants such as propane, butane, nitrogen, compressed air, dimethyl ether, carbon dioxide, nitrous oxide, or mixtures of these gases.

The oil spray formulations differ from the aerosol recipes in that no propellants are used.

- The compounds of formula I and its respective compositions can also be used in mosquito and fumigating coils, smoke cartridges, vaporizer plates or long-term vaporizers and also in moth papers, moth pads or other heat-independent vaporizer systems.
- The compounds of formula I are also suitable for the treatment of seeds. Conventional seed treatments include suspension concentrates FS and wettable powders WS.
 - The compounds of formula I can also be formulated into pour-on formulations.
- The following list of pesticides together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:
 - Organophosphates: Acephate, Azinphos-methyl, Chlorpyrifos, Chlorfenvinphos, Diazinon, Dichlorvos, Dicrotophos, Dimethoate, Disulfoton, Ethion, Fenitrothion, Fenthion, Isoxathion, Malathion, Methamidophos, Methidathion, Methyl-Parathion, Mevinphos, Monocrotophos, Oxydemeton-methyl, Paraoxon, Parathion, Phenthoate, Phosalone, Phosmet, Phosphamidon, Phorate, Phoxim, Pirimiphos-methyl, Profenofos, Prothiofos, Sulprophos, Triazophos, Trichlorfon;
- 35 Carbamates: Alanycarb, Benfuracarb, Carbaryl, Carbosulfan, Fenoxycarb, Furathiocarb, Indoxacarb, Methiocarb, Methomyl, Oxamyl, Pirimicarb, Propoxur, Thiodicarb, Triazamate;
- Pyrethroids: Bifenthrin, Cyfluthrin, Cypermethrin, Deltamethrin, Esfenvalerate, Ethofen-40 prox, Fenpropathrin, Fenvalerate, Cyhalothrin, Lambda-Cyhalothrin, Permethrin, Silafluofen, Tau-Fluvalinate, Tefluthrin, Tralomethrin, Zeta-Cypermethrin;

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Arthropod growth regulators: a) chitin synthesis inhibitors: benzoylureas: Chlorfluazuron, Diflubenzuron, Flucycloxuron, Flufenoxuron, Hexaflumuron, Lufenuron, Novaluron, Teflubenzuron, Triflumuron; Buprofezin, Diofenolan, Hexythiazox, Etoxazole, Clofentazine; b) ecdysone antagonists: Halofenozide, Methoxyfenozide, Tebufenozide; c) juvenoids: Pyriproxyfen, Methoprene, Fenoxycarb; d) lipid biosynthesis inhibitors: Spirodiclofen:

Various: Abamectin, Acequinocyl, Amitraz, Azadirachtin, Bifenazate, Cartap, Chlorfenapyr, Chlordimeform, Cyromazine, Diafenthiuron, Dinetofuran, Diofenolan, Emamectin, Endosulfan, Ethiprole, Fenazaquin, Fipronil, Formetanate, Formetanate hydrochloride, Hydramethylnon, Imidacloprid, Indoxacarb, Metaflumizon, Pyridaben, Pymetrozine, Spinosad, Sulfur, Tebufenpyrad, Thiamethoxam, and Thiocyclam.

The insects may be controlled by contacting the target parasite/pest, its food supply. 15 habitat, breeding ground or its locus with a pesticidally effective amount of compounds of or compositions of formula I.

"Locus" means a habitat, breeding ground, plant, seed, soil, area, material or environment in which a pest or parasite is growing or may grow.

In general, "pesticidally effective amount" means the amount of active ingredient needed to achieve an observable effect on growth, including the effects of necrosis, death, retardation, prevention, and removal, destruction, or otherwise diminishing the occurrence and activity of the target organism. The pesticidally effective amount can vary for the various compounds/compositions used in the invention. A pesticidally effective amount of the compositions will also vary according to the prevailing conditions such as desired pesticidal effect and duration, weather, target species, locus, mode of application, and the like.

The compounds of formula I and its compositions can be used for protecting wooden materials such as trees, board fences, sleepers, etc. and buildings such as houses, outhouses, factories, but also construction materials, furniture, leathers, fibers, vinyl articles, electric wires and cables etc. from ants and/or termites, and for controlling ants and termites from doing harm to crops or human being (e.g. when the pests invade into houses and public facilities). The compounds of formula I are applied not only to the surrounding soil surface or into the under-floor soil in order to protect wooden materials but it can also be applied to lumbered articles such as surfaces of the under-floor concrete, alcove posts, beams, plywoods, furniture, etc., wooden articles such as particle boards, half boards, etc. and vinyl articles such as coated electric wires, vinyl sheets, heat insulating material such as styrene foams, etc. In case of application against ants doing harm to crops or human beings, the ant controller of the present invention is ap-

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plied to the crops or the surrounding soil, or is directly applied to the nest of ants or the like.

The compounds of the invention can also be applied preventively to places at which 5 occurrence of the pests is expected.

The compounds of formula I may be also used to protect growing plants from attack or infestation by pests by contacting the plant with a pesticidally effective amount of compounds of formula I. As such, "contacting" includes both direct contact (applying the compounds/compositions directly on the pest and/or plant - typically to the foliage, stem or roots of the plant) and indirect contact (applying the compounds/compositions to the locus of the pest and/or plant).

In the case of soil treatment or of application to the pests dwelling place or nest, the 15 quantity of active ingredient ranges from 0.0001 to 500 g per 100 m², preferably from 0.001 to 20 g per 100 m².

Customary application rates in the protection of materials are, for example, from 0.01 g to 1000 g of active compound per m² treated material, desirably from 0.1 g to 50 g per m².

For use in bait compositions, the typical content of active ingredient is from 0.001 weight % to 15 weight %, desirably from 0.001 weight % to 5% weight % of active compound.

For use in spray compositions, the content of active ingredient is from 0.001 to 80 weights %, preferably from 0.01 to 50 weight % and most preferably from 0.01 to 15 weight %.

30 For use in treating crop plants, the rate of application of the active ingredients of this invention may be in the range of 0.1 g to 4000 g per hectare, desirably from 25 g to 600 g per hectare, more desirably from 50 g to 500 g per hectare.

For use in treating seeds, the typical rate of application is from 1 g to 500 g per kilo-35 gram of seeds, desirably from 2 g to 300 g per kilogram of seeds, more desirably from 10 g to 200 g per kilogram of seeds.

This invention also provides a method for treating, controlling, preventing and protecting warm-blooded animals, including humans, and fish against infestation and infection 40 by pests of the orders Siphonaptera, Hymenoptera, Hemiptera, Blattaria, Phthiraptera, and Diptera, which comprises orally, topically or parenterally administering or applying to said animals an pesticidally effective amount of compounds of formula I.

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The invention also provides a process for the preparation of a composition for treating, controlling, preventing or protecting a warm-blooded animal or a fish against infestation or infection by pests of the Siphonaptera, Hymenoptera, Hemiptera, Blattaria, Phthiraptera, and Diptera orders which comprises a pesticidally effective amount of a compound having the formula I.

The above method is particularly useful for controlling and preventing infestations and infections in warm-blooded animals such as cattle, sheep, swine, camels, deer, horses, poultry, rabbits, goats, dogs and cats as well as humans.

Infestations in warm-blooded animals and fish including, but not limited to, lice, biting lice, ticks, nasal bots, keds, biting flies, muscoid flies, flies, mylasitic fly larvae, chiggers, gnats, mosquitoes and fleas may be controlled, prevented or eliminated by the 15 compounds of formula I. The compounds of formula I are especially useful for combating pests of the following orders:

Siphonaptera, e.g. Ctenocephalidea felis, C. canis, Xenopsylla cheopis, Pulex irritans, Tunga penetrans, and Nosopsyllus fasciatus,

Hymenoptera: Solenopsis spp., S. invicta, S. richteri, S. xyloni, S. geminata, Pogomyrmex spp., P. barbatus, P. californicus, Dasymutilla occidentalis, Africanized honey bees, Bombus spp., Vespula squamosa, Paravespula vulgari, P. pennsylvanica, P. germanica, Dolichovespula maculata, Vespa crabro, and Polistes rubiginosa,

Hemiptera: Cimex lectularius, C. hemipterus, Reduvius senilis, Triatoma spp., and Arilus critatus.

Blattaria: Blattella germanica, B. asahinae, Blatta oriantalis, Periplaneta Americana, P. 30 fuliginosa, P. brunnea, and P. australasiae.

Phthiraptera: Pediculus humanus corporis, P. h. capitis, and Pthirus pubis,

Diptera: Aedes aegypti, A. albopictus, Anopheles crucinas, An. albimanus, An. Gam-35 biae, An. freeborni, An. leucosphyrus, An. minimus, An. quadrimaculatus, Culex nigripalpus, C. quinquefasciatus, C. tarsalis, Culiseta inornata, C. melanura, Mansonia titillanus, Psorophora columbiae, P. discolor, Prosimuliim mixtum, Simuliim vittatum, Chrysops discalis, C. silacea, C. atlanticus, Tabanus atratus, T. lineola, T. similes, Culicoides furens, Leptoconops torrens, Phlebotomus argentipes, Stomoxys calcitrans, 40 Glossina spp., G. palpalis, G. fuscipes, G. tachinoides, Musca domestica, Sarcophaga haemorrhoidalis, Calliphora vicina, Hippelates spp., Dermatobia hominis, Chrysomya bezziana, and Cochliomyia hominivorax.

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For oral administration to warm-blooded animals, the formula I compounds may be formulated as animal feeds, animal feed premixes, animal feed concentrates, pills, solutions, pastes, suspensions, drenches, gels, tablets, boluses and capsules. In addition, the formula I compounds may be administered to the animals in their drinking water. For oral administration, the dosage form chosen should provide the animal with 0.01 mg/kg to 100 mg/kg of animal body weight per day of the formula I compound.

Alternatively, the formula I compounds may be administered to animals parenterally, for example, by intraruminal, intramuscular, intravenous or subcutaneous injection. The formula I compounds may be dispersed or dissolved in a physiologically acceptable carrier for subcutaneous injection. Alternatively, the formula I compounds may be formulated into an implant for subcutaneous administration. In addition the formula I compound may be transdermally administered to animals. For parenteral administration, the dosage form chosen should provide the animal with 0.01 mg/kg to 100 mg/kg of animal body weight per day of the formula I compound.

The formula I compounds may also be applied topically to the animals in the form of dips, dusts, powders, collars, medallions, sprays and pour-on formulations. For topical application, dips and sprays usually contain 0.5 ppm to 5,000 ppm and preferably 1 ppm to 3,000 ppm of the formula I compound. In addition, the formula I compounds may be formulated as ear tags for animals, particularly quadrupeds such as cattle and sheep.

The formula I compounds of this invention may also be used in combination or conjunc-25 tion with one or more other parasiticidal compounds including, but not limited to, anthelmintics, such as benzimidazoles, piperazine, levamisole, pyrantel, praziquantel and the like; endectocides such as avermectins, milbemycins and the like; ectoparasiticides such as anylpyrroles, organophosphates, carbamates, gamabutyric acid inhibitors including fipronil, pyrethroids, spinosads, imidacloprid and the like; insect growth requ-30 lators such as pyriproxyfen, cyromazine and the like; and chitin synthase inhibitors such as benzoylureas including flufenoxuron.

Examples of action against pests

35 Test Methodology

1. Activity against argentine ant, harvester ant, acrobat ant, carpenter ant, fire ant, house fly, stable fly, flesh fly, yellowfever mosquito, house mosquito, malaria mosquito. German cockroach, cat flea, and brown dog tick via glass contact

Glass vials (20 ml scintillation vials) were treated with 0.5 ml of a solution of active ingredient in acetone. Each vial was rolled uncapped for ca. 10 minutes to allow the a.i.

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to completely coat the vial and to allow for full drying of the acetone. Insects or ticks were placed into each vial. The vials were kept at 22 °C and were observed for treatment effects at various time intervals. Results are presented in Table 1.

5 2. Activity against argentine ant, acrobat ant, carpenter ant, fire ant, and eastern subterranean termite via soil contact

For ants, tests were conducted in Petri dishes. A thin layer of 1 % agar in water was dispensed into the dishes and Florida sandy soil was spread over the agar (5 g for the small dishes and 11 g for the larger dishes). The active ingredient was dissolved in acetone and dispensed over the sand. Dishes were vented to evaporate the acetone, infested with ants, and covered. A 20% honey water solution was placed in each dish. The dishes were maintained at 22°C and observed for mortality at various time intervals.

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For termites, a thin layer of 1% agar was dispensed into Petri dishes. A thin layer of pre-treated soil was spread over the agar. For soil treatment, the active ingredient was diluted in acetone on a weight-to-weight basis and incorporated into 100 g of soil. The soil was placed in a jar and vented for 48 hours. The moisture level of the soil was brought to field capacity by adding 7 ml of water. Termite workers were introduced into each dish. A small piece of filter paper was placed into each dish after 1 day as a food source, and additional water was added as needed to maintain soil moisture. Test dishes were held at a dark incubator at 25°C and 80% room humidity. Termites were observed daily for mortality (dead or unable to stand upright and showing only weak movement). Results are shown in Table 1.

3. Activity against argentine ant, acrobat ant, carpenter ant, fire ant, house fly, eastern subterranean termite, formosan subterranean termite, and German cockroach via bait

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For argentine ant, acrobat ant, and carpenter ant, tests were conducted in Petrl dishes. Ants were given a water source, and then were starved of a food source for 24 hours. Baits were prepared with either 20% honey/water solutions or ground cat chow. Active ingredient in acetone was added to the bait. 0.2 ml of treated honey water solution or 150 mg of treated cat chow, placed in a cap, was added to each dish. The dishes were covered and maintained at a temperature of 22°C. The ants were observed for mortality daily. Results are shown in Table 1.

For the fire ants, corn grit was used as a bait matrix. Corn grit bait was prepared using a mixture of defatted corn grit (80%), soybean oil (19.9%), acetone, and the active ingredient (0.1%). Petri dishes were supplied with a water source. Fire ant adults were

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placed into each dish. The next day, 250 mg of bait in bait containers was placed into the dishes. The ants were observed for mortality daily. Results are shown in Table 1.

For house flies. Bait tests were conducted with adults aged 2-5 days post-emergence. Active ingredient in acetone was applied to a bait matrix consisting of a 1:1 mixture of powdered milk and sugar which was then allowed to dry. Assays were conducted in jars with 250 mg of bait in a pan placed in the bottom of each jar. House flies were placed into the bait jars which were covered. The test jars were held at 22°C. Test jars were observed at 4 and 24 hours after treatment for knockdown and 2 and 3 days after treatment for knockdown (death plus morbidity (unable to stay upright) plus intoxication (able to stand but unable to fly). Results are shown in Table 1.

For termites, active ingredient in acetone was applied to filter papers. % a.i. were calculated on basis of the weight of the filter paper. Acetone only was applied for untreated controls. Treated papers were vented to evaporate the acetone, moistened with ml water, and placed Petri dishes with sand. Water was added during the test as needed. Bioassays were conducted with one treated filter and ca. 30 termite workers per test dish. Test dishes were maintained at 25°C and 85% room humidity and observed daily for mortality (dead or moribund insects) or intoxication. Dead or moribund insects were removed daily. Results are shown in Table 1.

For cockroaches, plastic roach boxes with ventilated lids were used as test arenas. The top 3-4 cm of the arenas was treated with Vaseline and mineral oil to prevent roaches from escaping. Water was provided as needed. The bait was prepared using ground cat chow, and the active ingredient in acetone was incorporated on a weight- to-weight ratio. The treated chow was allowed to dry. The cockroaches were placed in the boxes and starved for 24 hours prior to bait introduction. 0.03 grams of bait per box were placed in a weigh boat. The boxes were maintained at 22°C and observed daily for mortality of the cockroaches. Results are shown in Table 1.

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4. Activity against yellowfever mosquito, southern house mosquito, and malaria mosquito larvae via water treatment

Well plates were used as test arenas. The active ingredient was dissolved in acetone and diluted with water to obtain the concentrations needed. The final Solutions containing appr. 1% acetone were placed into each well. Approximately 10 mosquito larvae (4th-instairs) in 1 ml water were added to each well. Larvae were fed one drop of liver powder each day. The dishes were covered and maintained at 22°C. Mortality was recorded daily and dead larvae and live or dead pupae were removed daily. At the end of the test remaining live larvae were recorded and percent mortality was calculated. Results are shown in Table 1.

Each test was replicated at least 3 times.

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Results

Tests conducted with compounds of formula I-1 and I-2 showed the following results:

Table 1. Activity against various species.

Pest Common Name	Pest Latin Name	Rate	Days or Hours to	
			achieve 100% mortality	
Activity via glass contact	t	<u></u>		
argentine ant	Linepitheum humile	10 ppm	1-2 days	
harvester ant	Pogonomyrmex califor-	10 ppm	2-3 days	
	nicus			
acrobat ant	Crematogaster spp.	10 ppm	1-2 days	
carpenter ant	Camponotus floridanus	10 ppm	1 day	
fire ant	Solenopsis invicta	10 ppm	4 hours	
house fly	Musca domestica	10 ppm	4 hours	
stable fly	Stomoxys calcitrans	10 ppm	4 hours	
flesh fly	Sarcophaga sp.	10 ppm	4 hours	
yellowfever mosquito	Aedes aegypti	10 ppm	4 hours	
house mosquito	Culex quinquefasciatus	0.5 ppm	4 hours	
malaria mosquito	Anopheles albimanus	1 ppm	1 day	
german cockroach	Blattella germanica	100 ppm	5-24 hours	
cat flea	Ctenocephalides felis	100 ppm	2 days	
brown dog tick	Rhipicephalus san-	10 ppm	3-5 days	
	guineus]		
Activity via soil contact				
argentine ant	Linepitheum humile	0.1w%	1-2 days	
acrobat ant	Crematogaster spp.	0.01w%	2 days	
carpenter ant	Camponotus floridanus	0.01w%	1 day	
fire ant	Solenopsis invicta	0.01w%	1 day	
subterranean termite	Reticulitermes flavipes	0.005w%	1-3 days	
Activity via bait				
argentine ant	Linepitheum humile	1.0w%	2-3 days	
acrobat ant	Crematogaster spp.	1.5w%	6-7 days	
carpenter ant	Camponotus floridanus	2.0w%	1-3 days	
fire ant	Solenopsis invicta	0.7w%	3 days	
house fly	Musca domestica	0.1w%	3 hours	
subterranean termite	Reticulitermes flavipes	0.1w%	1-2 days	
formosan termite	Coptotermes formosa-	0.1w%	5 days	
	nus			

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Pest Common Name	Pest Latin Name	Rate	Days or Hours to achieve 100% mortality
german cockroach	Blattella germanica	0.3w%	1-2 days
Activity via water treatn	nent	<u> </u>	
yellowfever mosquito	Aedes aegypti	10 ppm	2 days
house mosquito	Culex quinquefasciatus	10 ppm	1 day
malaria mosquito	Anopheles albimanus	1.0 ppm	1 day

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Claims:

The use of compounds of formula I

$$\bigvee_{R=\Delta}^{n} - \bigvee_{N=Q}^{R} \qquad (I)$$

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wherein

Q

$$N = \stackrel{NR^1R^2}{=} , \qquad N = \stackrel{X^1}{=} , \text{ or } \qquad \stackrel{R^4}{\stackrel{1}{=}} \stackrel{O}{=}$$

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 X^1 is chlorine, bromine, or fluorine;

R¹, R² are each independently hydrogen, C₁-C₁₀-alkyl, C₃-C₁₀-alkenyl, C₃-C₁₀-alkynyl, or C₃-C₁₂-cycloalkyl, C₁-C₆-alkylamino, di(C₁-C₆alkyl)-amino, C1-C6-alkylcarbonylamino, C1-C6-alkylsulfonyl, or C1-C₆-alkylsulfinyl, wherein the carbon atoms in these groups may be substituted with

> 1 to 3 halogen, hydroxy, nitro, cyano, amino, mercapto, C₁-C₆alkoxy, C1-C6-haloalkoxy, C1-C6-alkylthio, C1-C6-haloalkylthio, C1-C6-alkylsulfonyl, C1-C6-alkylsulfinyl, C1-C6-haloalkylsulfonyl, C1-C6-haloalkylsulfinyl, or C3-C6-cycloalkyl which may be substituted with 1 to 3 R# groups, or

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R" is halogen, cyano, nitro, hydroxy, mercapto, amino, C1-C₈-alkoxy, C₂-C₆-alkenyloxy, C₂-C₆-alkynyloxy, C₁-C₆haloalkoxy, C1-C6-alkylthio, or C1-C6-haloalkylthio, C1-C6alkylsulfonyl, C1-Ce-alkylsulfinyl, C1-Ce-alkylamino, di(C1-C₆alkyl)-amino, C₁-C₆-alkylcarbonyl, C₁-C₆-alkoxycarbonyl, or di(C₁-C₆)-alkylaminocarbonyl;

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formyl, C₁-C₆-alkylcarbonyl, C(=O)NR^aR^b, CO₂R^c, R^d, R^e, phenyl which may be substituted with 1 to 3 R* groups, or pyridyl which may be substituted with 1 to 3 R# groups.

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Ra, Rb, Rc are each independently hydrogen or C1-C4-alkyl which may be substituted with 1 to 3 groups R":

 B_q is NRⁱR^j or

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$$N \stackrel{(CH_2)_p}{\swarrow} X_r$$
 or $CH \stackrel{(CH_2)_p}{\swarrow} X_r$

Rⁱ, Rⁱ are each independently hydrogen or C₁-C₄-alkyl which may be substituted with 1 to 3 groups R[#];

p, m are each independently 0, 1, 2, or 3, with the proviso that p and m are not both 0.

X is oxygen, sulfur, amino, C₁-C₄-alkylamino, or phenylamino, or, if p is 0 then X can also be phenoxy or C₁-C₆-alkoxy;

r is 0 or 1;

R^e is

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 R^k , R^q are each independently hydrogen or C_1 - C_4 -alkyl which may be substituted with 1 to 3 groups R^* ; or

R1 and R2 may be taken together to form a ring represented by the structure

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p,m are 1, 2 or 3;

X' is oxygen, sulfur, amino, C₁-C₄-alkylamino, phenylamino, or methylene;

Z is C₁-C₄-alkyl or phenyl;

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R³ is hydrogen, C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₃-C₁₂-cycloalkyl, wherein the carbon atoms in these groups may be partially or fully halogenated or substituted with

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1 to 3 cyano, nitro, hydroxy, mercapto, amino, C_1 - C_8 -alkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylamino, di(C_1 - C_6 -alkyl)-amino, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylsulfonyl, or C_1 - C_8 -alkylsulfinyl groups, wherein the carbon atoms in these groups may be substituted by

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1 to 3 halogen atoms, a 5- to 6-membered aromatic ring system which may contain 1 to 4 heteroatoms selected from

5	oxygen, sulfur and nitrogen and which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C_1 - C_6 -alkyl, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylsulfonyl, C_1 - C_6 -alkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms, or
10	phenoxy, which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C_1 - C_8 -alkyl, C_1 - C_6 -alkylsulfonyl, C_1 - C_6 -alkylsulfinyl, C_1 - C_6 -alkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms, or
15	a 3- to 6-membered saturated or partially unsaturated ring system which contains 1 to 3 heteroatoms selected from oxygen, sulfur and nitrogen and which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C ₁ -C ₆ -alkyl, C ₁ -C ₆ -alkylthio, C ₁ -C ₅ -alkylsulfonyl, C ₁ -C ₆ -alkylsulfinyl,
20	C_1 - C_6 -alkoxy, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted by 1 to 3 halogen atoms,
25 .	a 3- to 6-membered saturated or partially unsaturated ring system which contains 1 to 3 heteroatoms selected from oxygen, sulfur and nitrogen and which is unsubstituted or substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C ₁ -C ₆ -alkyl, C ₁ -C ₆ -alkylthio, C ₁ -C ₆ -alkylsulfonyl, C ₁ -C ₆ -alkylsulfinyl, C ₁ -C ₆ -alkylsulfonyl, C ₁ -C ₆ -alkylsulfon
30	bon atoms in these groups may be substituted by 1 to 3 halogen atoms;
	R, R ⁴ are each independently hydrogen or C ₁ -C ₆ -alkyl, C ₁ -C ₆ -alkyl)-alkoxycarbonyl, C ₁ -C ₆ -alkylaminocarbonyl, or di(C ₁ -C ₆ -alkyl)-aminocarbonyl, wherein the carbon atoms in the these groups may be
35	substituted with 1 to 3 groups R*;

with the proviso that one of A, B and W is other than N;

is C-R⁵ or N;

is C-R⁶ or N;

is C-R7 or N;

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R⁵, R⁶, R⁷ are each independently hydrogen, halogen, nitro, cyano, amino, mercapto, hydroxy, C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-alkylamino, di(C₁-C₆-alkyl)-amino, C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, or C₁-C₅-alkylsulfinyl, wherein the carbon atoms in these groups may be substituted with 1 to 3 groups R*

a 5- to 6-membered aromatic ringsystem which may contain 1 to 4 heteroatoms selected from oxygen, sulfur and nitrogen and which may be substituted with any combination of 1 to 5 halogen atoms, 1 to 3 C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_1 - C_6 -alkylsulfonyl, C_1 - C_6 -haloalkylsulfonyl, C_1 - C_6 -haloalkylsulfonyl, C_1 - C_6 -haloalkylsulfonyl, C_1 - C_6 -haloalkoxy, mercapto, hydroxy, amino, nitro, or cyano groups, wherein the carbon atoms in these groups may be substituted with 1 to 3 groups R^* ;

Y is hydrogen, halogen, cyano, nitro, amino, hydroxy, mercapto, C₁-C₆-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₅-alkylamino, di(C₁-C₆)-alkylamino, C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, or C₁-C₆-alkylsulfinyl, wherein the carbon atoms in these groups may be substituted with 1 to 3 groups R*;

n is 0, 1, or 2;

or the enantiomers or diastereomers, salts or esters thereof,

for combating non-crop pests.

2. The use according to claim 1 of compounds of formula I as defined in claim 1 wherein

A is C-R⁵;

B is C-R⁶; and

W is C-R⁷.

3. The use according to claim 1 wherein the compound of formula I is a compound of formula I-1 or I-2.

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- The use according to any one of claims 1 to 3 wherein the non-crop pests are 4. selected from the Isoptera, Diptera, Blattaria (Blattodea), Hymenoptera, and Siphonaptera orders.
- 5 The use of compounds as defined in any one of claims 1 to 3 for protecting 5. wooden materials against pests from the Isoptera and Hymenoptera orders.
 - 6. A method for controlling non-crop pests comprising contacting the pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of a compound of formula I as defined in any one of claims 1 to 3.
 - 7. A bait composition which comprises a compound of formula I as defined in any one of claims 1 to 3 and a food stimulant.
- 15 8. A method for treating, controlling, preventing or protecting a warm-blooded animal or a fish against infestation or infection by pests of the orders Siphonaptera, Hymenoptera, Hemiptera, Blattaria, Phthiraptera and Diptera which comprises orally, topically or parenterally administering or applying to said animal or fish a pesticidally effective amount of a compound having the formula I as defined in any one of claims 1 to 3. 20
- A process for the preparation of a composition for treating, controlling, preventing 9. or protecting a warm-blooded animal or a fish against infestation or infection by the Siphonaptera, Hymenoptera, Hemiptera, Blattaria, Phthiraptera and Diptera 25 orders which comprises a pesticidally effective amount of a compound of formula I as defined in any one of claims 1 to 3.

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Abstract

The use of compounds of formula I

$$\bigvee_{N=A}^{n} \bigvee_{N-Q}^{R} \qquad (I)$$

wherein Q is

$$N = \stackrel{NR^1R^2}{R^3}$$
, $N = \stackrel{X^1}{R^3}$, or $\stackrel{R^4}{N} = \stackrel{O}{R^3}$.

X1 is halogen;

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R¹ and R² are each H, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, alkylamino, dialkyl-amino, alkylcarbonylamino, alkylsulfonyl, or alkylsulfinyl, or R¹ and R² may be taken together to form a ring represented by the structure below, wherein p,m are 1, 2 or 3, X' is O, S, NH, alkylamino, phenylamino, or methylene, Z is alkyl or phenyl;

R3 is H or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl,

R. R⁴ are each H, or optionally substituted alkyl, alkoxycarbonyl, alkylaminocarbonyl, or dialkylaminocarbonyl,

A is C-R⁵ or N; B is C-R⁶ or N; W is C-R⁷ or N; with the proviso that one of A, B and W must be other than N;

R⁵, R⁶, R⁷ are each H, halogen, NO₂, CN, NH₂, SH, OH, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkylsulfonyl, or alkylsulfinyl, or a 5- to 6-membered optionally substituted aromatic ring system which may contain 1 to 4 heteroatoms selected from oxygen, sulfur and nitrogen Y is H halogen, CN, NO₂, NH₂, OH, SH, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkylsulfonyl, or alkylsulfinyl, n is 0, 1, or 2;

or the enantiomers or diastereomers, salts or esters thereof, for combating pests and compositions comprising compounds I.